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Molecular catalytic system for efficient water splitting

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Mono Ruthenium Catalysts for Water Splitting

ABSTRACT

A class of single site homogeneous water splitting catalysts is presented in this chapter that shows for the first time a four-step proton coupled electron transfer (PCET) pathway for molecular oxygen generation by a bifunctional proton management mechanism to stabilize a divalent catalyst complex during the four-electron water oxidation cycle. The *p*-cymene mononuclear ruthenium derived water oxidation complexes with dinitrogen ligands are easily accessible and relatively inexpensive compared to other available ruthenium complexes. The aqua exchange induction step levels the chemical potential in the PCET water oxidation cycle by facilitating the proton release. Since water ligation contributes with two hydrogen atoms, it activates the complex for two consecutive PCET steps with a very similar proton management system. The aqua ligation of the $[\text{Ru}^{\text{IV}}(\text{=O})]^{2+}$ complex at the beginning of the second half of the catalytic cycle is facilitated by a large bite angle and a wide coordination gap between the dinitrogen ligand bound to Ru and the aromatic moiety. A mechanism is proposed where the donating *p*-cymene stabilizes the $[\text{Ru}^{\text{IV}}(\text{=O})]^{2+}$ state and prevents its further oxidation to the $[\text{Ru}^{\text{V}}(\text{=O})]^{3+}$ complex before second OH_2 insertion. In this way the catalyst cycles through $\text{Ru}^{\text{III/IV}}-\text{Ru}^{\text{III/IV}}$ states with two water molecules coordinating sequentially while maintaining an overall charge +2. The free energy differences while going from HO^* to HOO^* are 3.1, 3.13 and 3.08 eV for $[(\text{cy})\text{Ru}^{\text{II}}(\text{bpy})\text{OH}_2]^{2+}$, $[(\text{cy})\text{Ru}^{\text{II}}(\text{phen})\text{OH}_2]^{2+}$ and $[(\text{cy})\text{Ru}^{\text{II}}(\text{bpm})\text{OH}_2]^{2+}$ complexes respectively, which is well in line with the free energy difference determined for a wide range of catalysts and within the standard range of 3.2 ± 0.1 eV [1].

Based on: K.S. Joya and H.J.M. de Groot, 2011 (*to be submitted*)

3.1. INTRODUCTION

Hydrogen generation from water splitting is difficult, and an efficient oxygen evolving complex that can be widely applied is still missing [1-3]. In particular, the development of a molecular system operating at moderate activation energies with high activity and rate for oxygen evolution is challenging from a catalytic standpoint [4-9]. It is well established that a four step PCET pathway is a key element for an efficient operation of the oxygen evolving complex (OEC) in natural photosynthesis, and the oxo-manganese cluster embedded in photosystem-II (PS-II) provides insight for the design of artificial substitutes [10-13]. Mono site ruthenium and iridium complexes have been reported that are active for water oxidation without a four step PCET reaction coordinate for oxygen evolution [13-15]. For the single-site ruthenium systems steric crowding reduces the accessibility of the complex for catalysis. In parallel, a relatively strong electron affinity of the tri-nitrogen ligands induces the formation of a $[\text{Ru}^{\text{V}}(\text{=O})]^{3+}$ complex by one electron oxidation of $[\text{Ru}^{\text{IV}}(\text{=O})]^{2+}$ [15,16]. As the formation of the $[\text{Ru}^{\text{V}}(\text{=O})]^{3+}$ complex is not coupled to deprotonation of the complex with the second OH_2 , the net build up of positive charge limits the maximum attainable rate, even in aqueous solution at higher pH [7].

A successive four-step PCET for the entire complex is a prerequisite for an optimal catalyst, since it facilitates the build up of redox equivalents by circumventing the high energy intermediates during multi-electron water splitting [12-14]. From a thermodynamics perspective, an ideal water oxidation catalyst operates along a reaction coordinate with an equilibrium potential of 1.23 V for each intermediate oxidation step [14,17]. The total free energy change for the formation of oxygen from H_2O is 4.92 eV, which is realized by the extraction of four electrons and protons by consecutive PCET steps from two water molecules [17,18]. In oxo-bridged binuclear ruthenium complexes, the oxygen formation proceeds via nucleophilic attack of OH_2 on the oxo ligand to generate the higher energy HOO^* intermediate [19,20]. Among the various intermediates that can be

produced during catalysis by mono-site systems, the formation of the peroxide (HOO^*) from $[\text{Ru}^{\text{IV}}=\text{O}]^{2+}$ acquires high energy since it is thought to proceed by a non-PCET step with a prior conversion into $[\text{Ru}^{\text{V}}=\text{O}]^{3+}$ instead of second aqua ligation and PCET to maintain a Ru^{IV} species [15,16].

The catalyst bound HOO^* intermediate produced in the second half of the water oxidation cycle is difficult to oxidize compared to the hydroxide (HO^*) in the first catalytic PCET step. It has been found empirically that there is an energy difference of 3.2 ± 0.1 eV between the HOO^* and HO^* intermediates along the catalysis pathway [14,17]. Depending on the chemical nature of the catalyst, either the $=\text{O}$ intermediate or the $-\text{OOH}$ transition determines the overall energy for the four-electron water oxidation process, and the free energy of the $=\text{O}$ intermediate can vary among catalysts, relative to the average of the positioning of the $-\text{OH}$ and the $-\text{OOH}$ intermediates on the reaction coordinate [17,18].

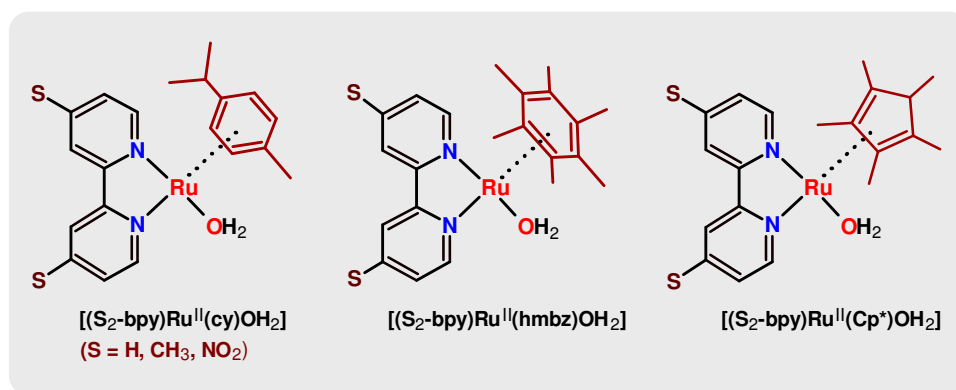


Figure 3.1. Ruthenium *p*-cymene (cy), hexamethyl benzene (hmbz) or pentamethyl-cyclopentadiene (Cp*) derived simple and 4,4'-disubstituted-2,2'-bipyridine, phenanthroline or bipyrimidine mono nuclear complexes [21].

This chapter describes a class of *p*-cymene (cy) derived single site ruthenium complexes (Fig. 3.1). The water splitting system for homogeneous catalysis is derived from Ru-cy complexes that are chemically preprogrammed with the bidentate ligands (L) like simple 2,2'-bipyridine (bpy) and 4,4'-disubstituted 2,2'-bipyridine ($\text{S}_2\text{-bpy}$), 1,10-phenanthroline (phen) and 2,2'-bipyrimidine (bpm) for

enhanced electron donation to the metal core from the aromatic moiety [21]. In combination with aqua ligation this produces a push-pull mechanism that can stabilize the $[\text{Ru}^{\text{IV}}(\text{=O})]^{2+}$ state by partial charge transfer from the ligand in synergy with deprotonation. This prevents the further oxidation into $[\text{Ru}^{\text{V}}(\text{=O})]^{3+}$ and facilitates the insertion of a second water molecule to the $[\text{Ru}^{\text{IV}}(\text{=O})]^{2+}$ intermediate. It provides the first example of the formation of the $[\text{Ru}^{\text{III}}(\text{OOH})]^{2+}$ species from a $[\text{Ru}^{\text{IV}}(\text{=O})]^{2+}$ complex by a PCET mechanism (Scheme 3.1). Homogeneous catalytic water oxidation was realized in aqueous acids in the presence of Ce(IV) as a one-electron oxidizing agent [16].

3.2. RESULTS AND DISCUSSION

3.2.1. Catalytic Complexes Synthesis and Characterization

The mono nuclear chloro complexes $[(\text{L})\text{Ru}^{\text{II}}(\text{cy})\text{Cl}]^+$ (**Ru-L**) were obtained in good purity and high yield (~ 70 %) by stirring a mixture of the $[\text{RuCl}_2(p\text{-cymene})]_2$ dimer with the respective ligand in methanol or acetone. The orange complexes were isolated and further purified by reprecipitation from acetone or methanol solution. The simple and 4,4'-disubstituted-2,2'-bipyridine, phen or bpm coordinate to the ruthenium upon cleavage of the dichloride bridge of the $[\text{RuCl}_2(p\text{-cymene})]_2$ dimer [22,23]. The purity and composition of the complexes were analyzed by proton NMR and by elemental analysis (see Materials and Methods for details and Fig. A3.1).

The exchange of the negatively charged chloride anion with a neutral aqua molecule in chloro complexes $[(\text{L})\text{Ru}^{\text{II}}(\text{cy})\text{Cl}]^+$ is accompanied by a colour change from orange-yellow to bright-yellow that was be followed in time with UV-vis spectroscopy (Fig. 3.2). The crystal structures of the similar complexes have been determined by X-ray diffraction and revealed a trans configuration of the dinitrogen ligand with respect to the *p*-cymene [23-25]. This structural configuration has a wide coordination gap between the bpy-Ru and the *p*-cymene ligand [24]. The aqua versions $[(\text{L})\text{Ru}^{\text{II}}(\text{cy})\text{-OH}_2]^{2+}$ (Cat.**Ru-L**) of the chloro

complexes were readily obtained, either *in situ* by dissolving in aqueous solution, or by stirring with stoichiometric aliquots of aqueous AgNO₃ or AgPF₆ in a methanol-water mixture.

3.2.2. Optical Measurements and Electrochemical Studies

The aqua exchange in [(bpy)Ru^{II}(cy)-Cl]⁺ (**Ru**-bpy) is accompanied by a colour change from orange-yellow to bright-yellow for the [(bpy)Ru^{II}(cy)-OH₂]²⁺ catalyst (Cat.**Ru**-bpy), as indicated by a pronounced change of the optical absorption profile in the spectral region between 300 nm and 500 nm (Fig. 3.2). Above pH=9, a broad band appears between 420 nm and 525 nm, indicating the deprotonated complex [(L)Ru^{II}(cy)-OH]⁺ in the alkaline medium. This is accompanied by a colour change from yellow to light-brown and darkening of the colour on further pH increase. These colour changes are attributed to exchange of chloride by a neutral water molecule at the catalytic ruthenium sites in the aqueous medium, followed by deprotonation of OH₂ into HO⁻, depending on the pH of the solution.

The cyclic voltammetry of the mono ruthenium complexes with [(terpy)-Ru-(N-N)]ⁿ⁺ and [(Mebimpy)-Ru-(N-N)]ⁿ⁺ scaffolds (terpy is 2,2':6'',2''-terpyridine; Mebimpy is 2,6-bis(1-methylbenzimidazol-2-yl)-pyridine ligand; N-N is 2,2'-bipyridine, 2,2'-bipyrimidine or 2,2'-bipyrazine), reveals two primary oxidation steps. For the Mebimpy-Ru-bpy complex, the reaction proceeds via two consecutive PCET steps generating the two Ru redox couples [Ru^{III}-(OH)]²⁺/[Ru^{II}-(OH₂)]²⁺ and [Ru^{IV}(=O)]²⁺/[Ru^{III}-(OH)]²⁺ at 0.81 V and 1.27 V (vs. NHE) respectively (pH=1) [7,15,16]. The two transitions show an approximately 60mV/pH shift while moving from an acidic to alkaline solution of pH~11-12. Further increase of the electrode potential produced a third oxidation of the catalytic site to form a [Ru^V(=O)]³⁺ type complex from [Ru^{IV}(=O)]²⁺ at > 1.67 V for [(Mebimpy)-Ru-(bpy)]ⁿ⁺ and at *ca.* 1.80 V for [(terpy)-Ru-(bpy)]ⁿ⁺ just before the second water insertion (Table 3.1). This oxidation is thought to be only an electron removal process, and water ligation is required to enable the proton release in a [Ru^{III}-(OOH)]²⁺/[Ru^V(=O)]³⁺ couple [16,19].

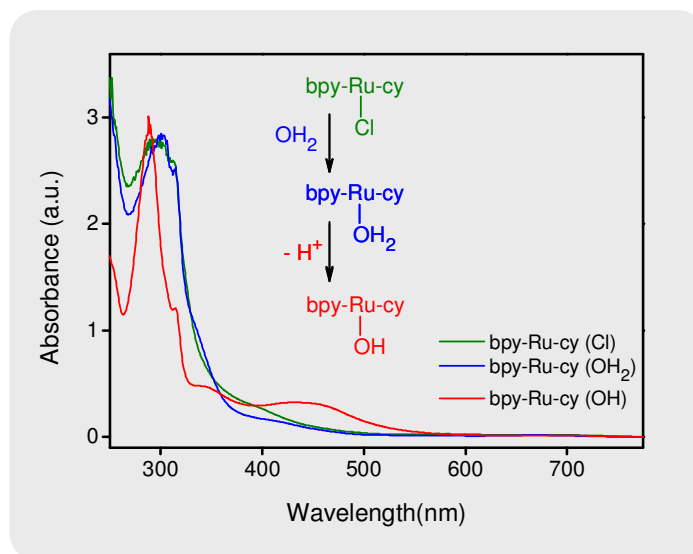


Figure 3.2. Electronic absorption spectra of the $[(bpy)Ru(cy)-(Cl)]^+$ complex (green line) following blue curve attributed to the formation of $[(bpy)Ru(cy)-(OH_2)]^{2+}$ catalyst induced by aqua exchange and deprotonation of the aqua $[(bpy)Ru(cy)-(OH_2)]^{2+}$ complex to form $[(bpy)Ru(cy)-(OH)]^+$ (red line). For all measurements a concentration of the complex of 7.5×10^{-5} M was used.

In this study, CV measurements for the complexes $[(bpy)Ru(cy)-(OH_2)]^{2+}$, $[(bpm)Ru(cy)-(OH_2)]^{2+}$ and $[(phen)Ru(cy)-(OH_2)]^{2+}$ were performed with a scan rate of 100 mV per second to avoid the weak polarization signals due to slow electrode kinetics of ruthenium oxidation in the complex that could occur at lower scan rate [16,26]. The current waves for the redox pairs $[Ru^{III}-(OH)]^{2+}/[Ru^{II}-(OH_2)]^{2+}$ and $[Ru^{IV}(=O)]^{2+}/[Ru^{III}-(OH)]^{2+}$ are observed around 0.51 – 0.61 V and 1.15 – 1.20 V (pH=1), respectively. The electrochemistry of Cat.**Ru**-bpy in aqueous acid reveals polarization waves for $[Ru^{III}-(OH)]^{2+}/[Ru^{II}-(OH_2)]^{2+}$ and $[Ru^{IV}(=O)]^{2+}/[Ru^{III}-(OH)]^{2+}$ representing two consecutive PCET steps as established before for mono ruthenium polypyridyl complexes [16,19]. These first two oxidation steps for the catalytic cycle of $[(bpy)Ru(cy)-(OH_2)]^{2+}$ appear at $E_{1/2}$ *ca.* 0.55 V and 1.19 V vs. NHE (Fig. A3.2a).

Further cycling of the potential leads to the formation of $[\text{Ru}^{\text{III}}-(\text{OOH})]^{2+}$ from the $[\text{Ru}^{\text{IV}}(=\text{O})]^{2+}$ species on the second aqua ligation, which is visible as a shoulder just above *ca.* 1.65 V, irreversible and superimposed on the background signal (Fig. A3.2a). This is followed by $[\text{Ru}^{\text{IV}}-(\text{OO})]^{2+}/[\text{Ru}^{\text{III}}-(\text{OOH})]^{2+}$ conversion with subsequent oxygen release above 1.81 V, observed as tiny bubbles on the working electrode surface during forward scans. The sequential oxidation of the $[\text{Ru}^{\text{II}}-\text{OH}_2]^{2+}$ complex into $[\text{Ru}^{\text{III}}-(\text{OH})]^{2+}$, $[\text{Ru}^{\text{IV}}(=\text{O})]^{2+}$ and the peroxo intermediate $[\text{Ru}^{\text{III}}-(\text{OOH})]^{2+}$ was also monitored spectro-photometrically by titrating with stoichiometric aliquots of cerium ammonium nitrate (CAN) and observing the absorption in the 275-400 nm range (Fig. A3.3). The spectral changes are consistent with the generation of the $[\text{Ru}^{\text{III}}-(\text{OH})]^{2+}$, $[\text{Ru}^{\text{IV}}(=\text{O})]^{2+}$ redox pairs in the first half and $[\text{Ru}^{\text{III}}-(\text{OOH})]^{2+}$ and $[\text{Ru}^{\text{IV}}-(\text{OO})]^{2+}$ species in the second part of the water oxidation cycle, as reported earlier for $[\text{terpy-Ru}-(\text{N-N})]^{n+}$ type mono nuclear complexes [15,16].

In neutral solution, $[\text{Ru}^{\text{III}}-(\text{OH})]^{2+}/[\text{Ru}^{\text{II}}-(\text{OH}_2)]^{2+}$ and $[\text{Ru}^{\text{IV}}(=\text{O})]^{2+}/[\text{Ru}^{\text{III}}-(\text{OH})]^{2+}$ intermediates exhibit quasireversible transitions and produce relatively weak polarization currents (Fig. A3.2b). This is attributed to slow reversible electrode kinetics of the complex on the electrode in the neutral phase and to electroprecipitation effects in the phosphate buffer solution [26]. The electrochemical data for the catalyst in aqueous solution confirm that two redox couples, $[\text{Ru}^{\text{III}}-(\text{OH})]^{2+}/[\text{Ru}^{\text{II}}-(\text{OH}_2)]^{2+}$ and $[\text{Ru}^{\text{IV}}(=\text{O})]^{2+}/[\text{Ru}^{\text{III}}-(\text{OH})]^{2+}$, produce a ~ 60 mV/pH shift characteristic of Nernst behaviour, while going from aqueous acid to a neutral solution (Fig. A3.2) and this validates the two consecutive PCET steps [19]. The electrochemical transition for $[\text{Ru}^{\text{III}}-(\text{OOH})]^{2+}/[\text{Ru}^{\text{IV}}(=\text{O})]^{2+}$ intermediate takes place at *ca.* 1.42 V (vs. NHE) during the forward scan in the neutral phase, while the reverse potential cycling reveals a reduction wave for the $[\text{Ru}^{\text{IV}}(=\text{O})]^{2+}/[\text{Ru}^{\text{III}}-(\text{OOH})]^{2+}$ couple at *ca.* 1.36 V vs. NHE (Fig. A3.2b). The pH dependence for the $[\text{Ru}^{\text{III}}-(\text{OOH})]^{2+}/[\text{Ru}^{\text{IV}}(=\text{O})]^{2+}$ transition is also consistent with Nernst behaviour for a third consecutive PCET step in the catalytic cycle of the $[(\text{bpy})\text{Ru}(\text{cy})-(\text{OH}_2)]^{2+}$ catalyst.

3.2.3. Pourbaix Diagrams

The Pourbaix diagrams (potential vs. pH plots) for the complexes were constructed from CV's obtained in aqueous solutions at various pH. The potential vs. pH plot for Cat.**Ru**-bpy is presented in Figure 3.3 and shows three pH-dependent current potential profiles with the characteristic Nernst slope of *ca.* 60 mV/pH for the observable ruthenium couples $[\text{Ru}^{\text{III}}(\text{-OH})]^{2+}/[\text{Ru}^{\text{II}}(\text{-OH}_2)]^{2+}$, $[\text{Ru}^{\text{IV}}(\text{=O})]^{2+}/[\text{Ru}^{\text{III}}(\text{-OH})]^{2+}$ and $[\text{Ru}^{\text{III}}(\text{-OOH})]^{2+}/[\text{Ru}^{\text{IV}}(\text{=O})]^{2+}$ (Figs. A3.4). The $[(\text{N-N})\text{Ru}^{\text{IV}}\text{=O}(\text{cy})]^{2+}$ complexes do not form the higher $[\text{Ru}^{\text{V}}(\text{=O})]^{3+}$ oxidation state complex that was reported recently for other classes of mono ruthenium catalysts and is generated at high potential, above 1.67 V (vs. NHE) at pH=1 [7,16]. The pH dependence of the potential for the $[\text{Ru}^{\text{III}}(\text{-OOH})]^{2+}/[\text{Ru}^{\text{IV}}(\text{=O})]^{2+}$ redox couple is attributed to insertion of a second water molecule at the $[(\text{N-N})\text{Ru}^{\text{IV}}\text{=O}(\text{cy})]^{2+}$ stage that makes it possible to avoid the further oxidation of the ruthenium core and the formation of a $[\text{Ru}^{\text{V}}(\text{=O})]^{3+}$ species [19]. The affinity of the $[\text{Ru}^{\text{IV}}(\text{=O})]^{2+}$ species for the coordination of the second water molecule is stabilized by the donating nature of the isopropyl and methyl substituted aromatic ligand towards the ruthenium centre.

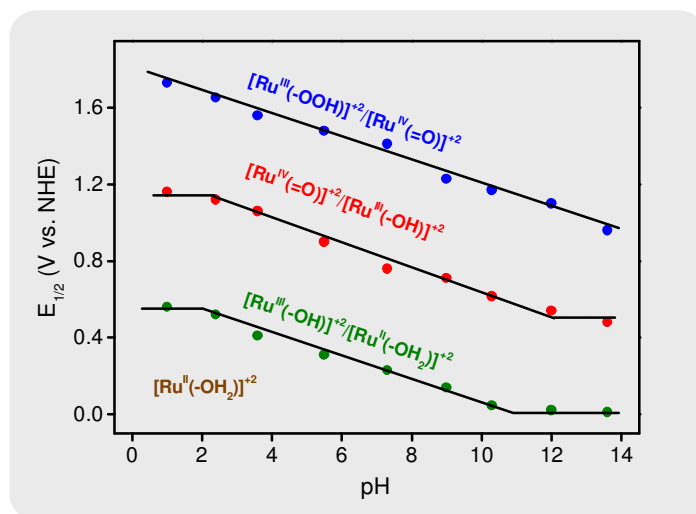


Figure 3.3. Pourbaix diagram for $[(\text{bpy})\text{Ru}^{\text{II}}(\text{OH}_2)(\text{cy})]^{2+}$ showing the ruthenium couples $[\text{Ru}^{\text{III}}(\text{-OH})]^{2+}/[\text{Ru}^{\text{II}}(\text{-OH}_2)]^{2+}$, $[\text{Ru}^{\text{IV}}(\text{=O})]^{2+}/[\text{Ru}^{\text{III}}(\text{-OH})]^{2+}$ and $[\text{Ru}^{\text{III}}(\text{-OOH})]^{2+}/[\text{Ru}^{\text{IV}}(\text{=O})]^{2+}$. The electrochemical data were generated from CV's obtained on a glassy carbon working electrode in 0.1 M aqueous solutions.

The large bite angle between bpy-Ru and the aromatic ligand that facilitates the aqua exchange in the catalyst induction step can promote second aqua ligation as well [22,23]. The higher oxidation state of the catalyst generated after ligation of a second water molecule is attributed to the $[\text{Ru}^{\text{III}}(\text{OOH})]^{2+}$ and $[\text{Ru}^{\text{IV}}(\text{OO})]^{2+}$ forms preceeding oxygen evolution [15]. Both higher potential ruthenium couples are produced by pH-dependent PCET oxidation of the $[\text{Ru}^{\text{IV}}(\text{=O})]^{2+}$ complex after insertion of the second water molecule, and without undergoing a transformation into a $[\text{Ru}^{\text{V}}(\text{=O})]^{3+}$ type species [16,19]. Hence this catalytic system exhibits a consecutive four step PCET oxidation process for water oxidation and molecular oxygen formation (Scheme 3.1). Thus, proton release is not rate-limiting and is accompanying the release of an electron in the ruthenium redox couples in $[(\text{N-N})\text{Ru}^{\text{II}}(\text{cy})\text{-OH}_2]^{2+}$ complexes. For all couples in the Pourbaix diagram the slope of ~ 60 mV/pH characteristic for PCET is observed, even at higher pH up to 12 (Fig. 3.3). This contrasts with the detection of a pH-dependent slope only for the first half of the cycle in mononuclear Ru catalysts with tri-nitrogen ligands and Ir-bpy derived water oxidation catalysts [7,8].

3.2.4. Free Energies of Intermediates Along the Reaction Coordinate for the Water Oxidation Cycle

The standard free energy changes (ΔG) associated with the HO^* , =O^* and HOO^* catalytic intermediates along the reaction coordinate for water oxidation and molecular oxygen formation for the $[(\text{cy})\text{Ru}^{\text{II}}(\text{bpy})\text{OH}_2]^{2+}$, $[(\text{cy})\text{Ru}^{\text{II}}(\text{phen})\text{OH}_2]^{2+}$ and $[(\text{cy})\text{Ru}^{\text{II}}(\text{bpm})\text{OH}_2]^{2+}$ complexes are calculated from the Pourbaix diagrams (pH=7) and transformed to a pH-independent reference frame that eliminates the 60 mV/pH shift. The total free energy change for the water oxidation process for an oxygen evolving catalyst operating at an optimal activity is $\Delta G = 4.92$ eV [18]. The dashed lines in Figure 3.4 represent the free energy levels for all intermediates of an optimal catalyst, with $\Delta G = 1.23$ eV for all four steps, similar to the natural PS-II [14,17]. For the HO^* , =O^* and HOO^* intermediates, the free energy levels are at 1.23 eV, 2.46 eV and 3.69 eV respectively. Catalytic water oxidation can proceed

when all steps are downhill [1]. With the three sequential intermediates for the Cat.**Ru**–bpy cycle at $\Delta G = 0.67, 1.27, 1.83$ eV (Fig. 3.4), and a total of 4.92 eV between the free energy of water and oxygen/hydrogen, the remaining free energy difference for the fourth step is $\Delta G = 1.15$ eV. The free energy profile for Cat.**Ru**–phen and Cat.**Ru**–bpm is given in the Figures A3.5.

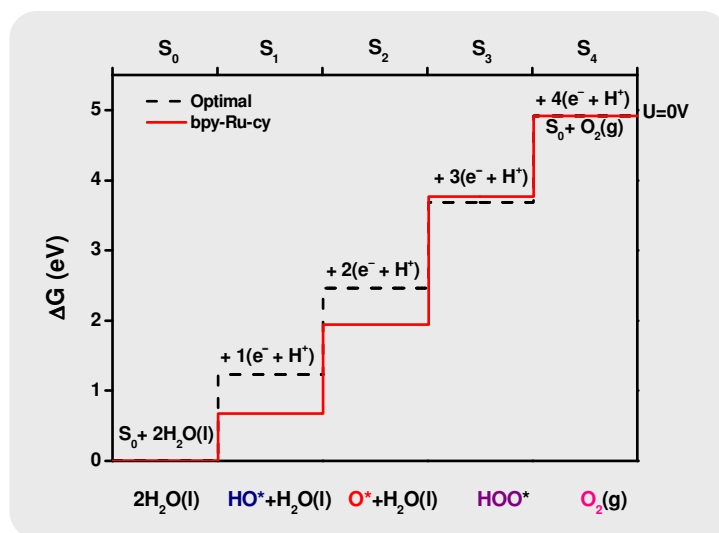


Figure 3.4. Relative Gibbs free energies (ΔG) of reactive species and intermediates along the reaction coordinate for water splitting and oxygen generation for the $[(\text{bpy})\text{Ru}^{\text{II}}(\text{OH}_2)(\text{cy})]^{2+}$ (Cat.**Ru**–bpy) [red solid line] catalytic system, compared with the free energy profile for an optimal catalyst (black dashed lines) with four equal steps of 1.23 eV [14,17].

The ΔG for the formation of the HOO^* species determines the activation barrier and gives rise to the overpotential, which is ~ 0.6 V for the three catalyst complexes, close to the theoretical minimum of 0.4 V overpotential for a mononuclear catalyst complex [17,18], suggesting that the $[(\text{cy})\text{Ru}^{\text{II}}(\text{bpy})\text{OH}_2]^{2+}$, $[(\text{cy})\text{Ru}^{\text{II}}(\text{phen})\text{OH}_2]^{2+}$ and $[(\text{cy})\text{Ru}^{\text{II}}(\text{bpm})\text{OH}_2]^{2+}$ complexes are good artificial catalysts for water splitting that operate via a four PCET step mechanism (Figs. A3.5). Rosmeissl *et al.* suggested that the free energy of the oxide intermediate can be adjusted independently of either HO^* or HOO^* , but normally the $=\text{O}$ intermediate or the $-\text{OOH}$ intermediate determines the overall energy for the four-

electron water oxidation process [1,17]. For mono-metal catalytic centers, the free energy difference between the HOO* and the HO* intermediate is 3.2 ± 0.1 eV [1]. The energy differences for the $[(\text{cy})\text{Ru}^{\text{II}}(\text{bpy})\text{OH}_2]^{2+}$, $[(\text{cy})\text{Ru}^{\text{II}}(\text{phen})\text{OH}_2]^{2+}$ and $[(\text{cy})\text{Ru}^{\text{II}}(\text{bpm})\text{OH}_2]^{2+}$ complexes are 3.1, 3.13 and 3.08 eV, respectively, well within the standard range [17,18].

3.2.5. Catalytic Water Oxidation

Catalytic homogeneous water oxidation was conducted *in situ* in an airtight glass cell and oxygen evolution was measured with a calibrated oxygen electrode connected to a digital oxygen-meter. The chloro complexes and catalysts Cat.**Ru**–bpy, Cat.**Ru**–dmbpy, Cat.**Ru**–dnbpy, Cat.**Ru**–phen and Cat.**Ru**–bpm are water soluble and addition of Ce(IV) in the form of CAN (cerium ammonium nitrate) leads to the detection of oxygen formation from water splitting. In a characteristic experiment, 350 equivalents of Ce(IV) were added to the Ar-purged aqueous solution of the catalysts in 0.1 M HNO₃.

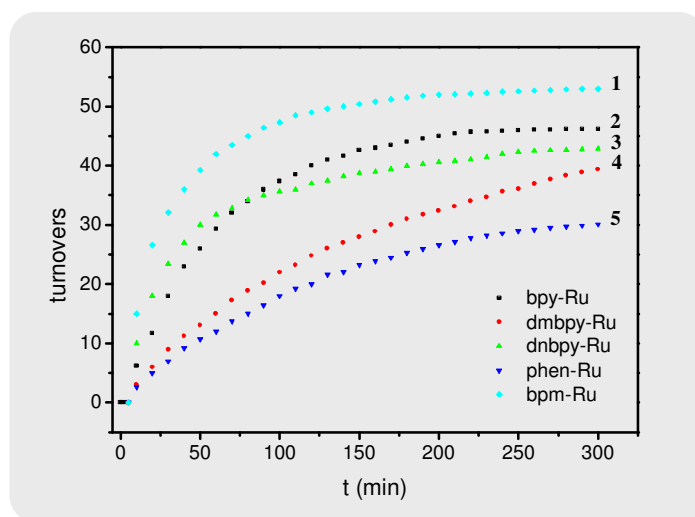


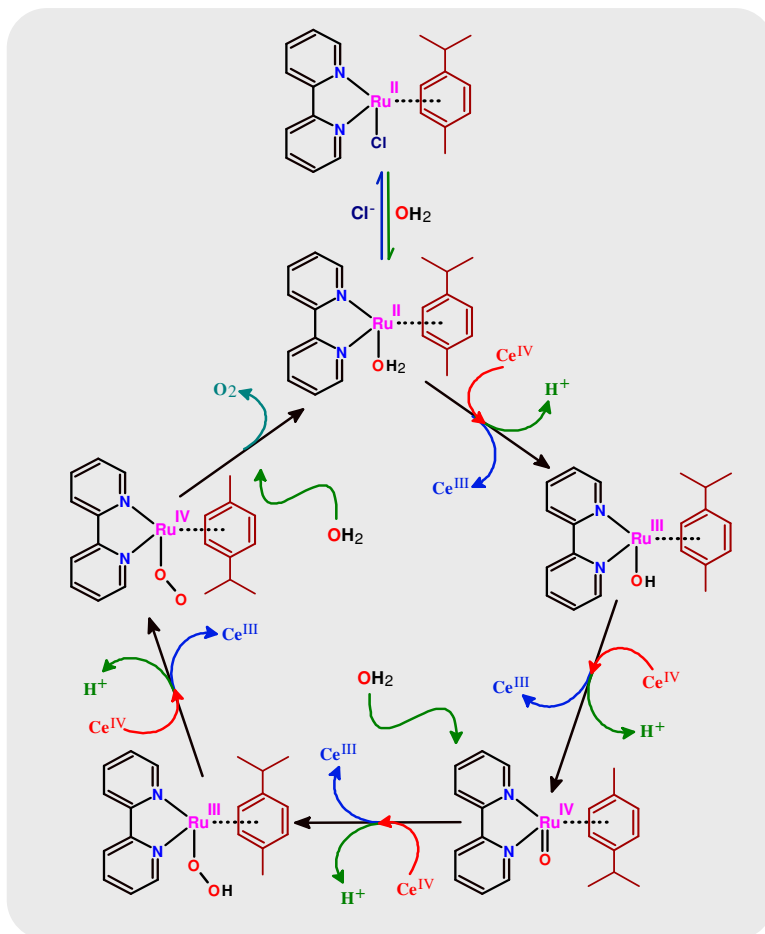
Figure 3.5. Oxygen turnovers vs. time during homogeneous water splitting catalysis by (1) $[(\text{cy})\text{Ru}^{\text{II}}(\text{bpm})\text{OH}_2]^{2+}$, (2) $[(\text{cy})\text{Ru}^{\text{II}}(\text{bpy})\text{OH}_2]^{2+}$, (3) $[(\text{cy})\text{Ru}^{\text{II}}(\text{dnbpy})\text{OH}_2]^{2+}$, (4) $[(\text{cy})\text{Ru}^{\text{II}}(\text{dmbpy})\text{OH}_2]^{2+}$ and (5) $[(\text{cy})\text{Ru}^{\text{II}}(\text{phen})\text{OH}_2]^{2+}$ with 350 eq. of Ce(IV) in aqueous deoxygenated 0.1 M HNO₃.

The oxygen generation turnovers obtained for Cat.**Ru**–L in 5 hours of catalysis are shown in Figure 3.5 (Table A3.1). Cat.**Ru**–bpm and Cat.**Ru**–dnbpy show a rapid initial oxygen generation rate with >40 and >30 turnovers respectively, in 50 minutes. The highest initial rapid response for catalytic oxygen evolution by the $[(\text{bpm})\text{Ru}^{\text{II}}(\text{OH}_2)(\text{cy})]^{2+}$ complex is ascribed to the presence of two nitrogen atoms in 2,2'-bipyrimidine that are more electron withdrawing compared to the two carbon atoms in the 4,4'-position of the 2,2'-bipyridine ligand [16].

3.2.6. Water Oxidation Mechanism

A postulated pentacyclic catalytic mechanism for water oxidation, based on electrochemical investigations of the $[(\text{L})\text{Ru}^{\text{II}}(\text{cy})\text{-OH}_2]^{2+}$ complex and potential vs. pH behaviour from the Pourbaix diagram, is presented in Scheme 3.1. First, aqua ligation of the $[(\text{L})\text{Ru}^{\text{II}}(\text{cy})\text{Cl}]^+$ complex in the catalyst induction step leads to the formation of a stable divalent $[(\text{L})\text{Ru}^{\text{II}}(\text{cy})\text{-OH}_2]^{2+}$ molecular species with a chemical topology or connectivity pattern that is different from the chloride precursor. Apparently the combination of electron donating properties of the *p*-cymene and the dinitrogen ligand produce a pK_a shift, sufficient to transform the OH^- into a lewis base that stabilizes the adduct with the H^+ , and leading to aqua ligation in a divalent form as opposed to OH^- ligation in a monovalent complex. Analogous forms of proton management have been encountered in biology, for instance in the complex counterion mechanism in the purple and blue forms of the transmembrane proton pump bacteriorhodopsin in the marine archebacterium *Halobacterium salinarium*, where the apparent pK_a is shifted by five units to stabilize a protonated species for light-driven biocatalysis and proton pumping in a concerted mechanism with a polyene electron donating moiety [28]. Thus, a bifactorial activation of the catalyst, a H_2X -Ru chemical topology in conjunction with a proton chemical potential bias, allows for two consecutive PCET steps. A PCET-ready species is formed by the addition of a proton that can be easily released again upon removal of an electron, while a second proton is also available for release upon extraction of a second electron by essentially the same mechanism.

Scheme 3.1. Proposed pentacyclic mechanism, based on electrochemical investigations, for homogeneous catalytic water oxidation by mono ruthenium $[(N-N)Ru^{II}(cy)-OH_2]^{2+}$ ($N-N$ = bpy, dmbpy, dnbpy, phen, bpm) catalysts. During the catalyst induction step, the $[(N-N)Ru^{II}(cy)-Cl]^{+}$ complexes are transformed into the corresponding aqua version by exchanging Cl^{-} with neutral OH_2 . Blue curved arrows represent four-step electron removal, with each step coupled to a proton transfer event, as indicated by green outward curved arrows. The oxidation states of the ruthenium possibly alternate through $Ru^{II}/Ru^{III}/Ru^{IV}-Ru^{III}/Ru^{IV}/Ru^{II}$, while maintaining an overall charge of +2. This is enabled by rapid association of a second water molecule, possibly accompanied by non rate-limiting internal rearrangements to generate $[Ru^{III}-(OOH)]^{2+}$ and $[Ru^{IV}-(OO)]^{2+}$ complexes by two successive PCET steps and eventually dioxygen release and water molecule insertion to recharge the system for the next catalytic cycle for water splitting and molecular oxygen evolution.



Subsequent insertion of a second water molecule re-establishes the proton management for the second half of the cycle and the activated form retains a double positive charge during the course of the whole catalytic cycle. Thus, on the addition

of Ce(IV) in the homogeneous phase, the $[(L)Ru^{II}(cy)-OH_2]^{2+}$ catalytic complexes lose two electrons in two stages, each coupled with a proton transfer event to form $[Ru^{III}-(OH)]^{2+}$ and $[Ru^{IV}(=O)]^{2+}$ consecutively. A wide coordination gap between the ruthenium bound dinitrogen ligand and the cymene probably provides a suitable environment for rapid second water molecule insertion with the catalytic sites, while the relatively strong electron donating property of the cymene aromatic ligand possibly prevents the formation of $[Ru^V(=O)]^{3+}$. This produces the first example of a $[Ru^{III}-(OOH)]^{2+}$ complex that operates fully with a four step PCET mechanism, similar to the natural PSII. The higher potential species, $[Ru^{III}-(OOH)]^{2+}$ and $[Ru^{IV}-(OO)]^{2+}$, are generated by two successive proton coupled electron transfer steps. Dioxygen is released from the $[Ru^{IV}-(OO)]^{2+}$ species on the addition of another water molecule, and this regenerates the $[(L)Ru^{II}(cy)-OH_2]^{2+}$ complex for the next catalytic cycle for water oxidation.

DFT calculations for ruthenium complexes with a tri-nitrogen ligand revealed that a seven-coordinate structure with a bidentate peroxide ligand is preferred over a six-coordinated structure with a terminal peroxido ligand [29,30]. In $[(L)Ru^{II}(cy)-OH_2]^{2+}$ type complexes, second aqua inclusion with a $[Ru^{IV}(=O)]^{2+}$ complex possibly generates a short lived non rate-limiting seven-coordinate Ru(IV/III) type intermediate. This structure then loses two electrons in two stages, each coupled with proton removal to realize a $[Ru^{III}-(OOH)]^{2+}$ complex, followed by $[Ru^{IV}-(OO)]^{2+}$ formation. Finally, the complex $[Ru^{IV}-(OO)]^{2+}$ releases the molecular oxygen on the inclusion of a water molecule. The above observations match the modified S-cycle for the natural Mn_4O_4Ca cluster [14]. Thus, a pH dependent four-electron cycle that is coupled with proton transfer enables to construct a mono metal water oxidation system (Scheme 3.1).

3.3. CONCLUSIONS

In conclusion, a group of mono site ruthenium derived molecular water splitting catalysts is presented here that devise a four step proton coupled electron transfer cycle for dioxygen formation in homogeneous conditions. The electrochemical data

for the complexes $[(\text{cy})\text{Ru}^{\text{II}}(\text{N-N})\text{-OH}_2]^{2+}$ are translated into the free energy difference, while going from HOO^* to HO^* intermediate, and show the values of 3.1, 3.13 and 3.08 eV for $[(\text{cy})\text{Ru}^{\text{II}}(\text{bpy})\text{OH}_2]^{2+}$, $[(\text{cy})\text{Ru}^{\text{II}}(\text{phen})\text{OH}_2]^{2+}$ and $[(\text{cy})\text{Ru}^{\text{II}}(\text{bpm})\text{OH}_2]^{2+}$ complexes, respectively. It is expected that the results presented here will contribute a novel mechanistic reaction process and knowledge for designing future water splitting systems for clean fuel generation. Further work on the development of complexes with other alkyl substituted benzene such as hexamethyl benzene or durene, and pentamethylcyclopentadiene with dinitrogen ligands, carboxylic acid derivatives of pyridine (COOH-py) and pyrazine (COOH-pz), and with N-Heterocyclic carbenes (NHC), is in progress.

3.4. MATERIALS AND METHODS

All syntheses of ligands and complexes were performed in oxygen free environment, in an argon or nitrogen atmosphere. $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ dimer, 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen), 2,2'-bipyrimidine (bpm), 4,4'-dimethyl-2,2'-bipyridine (dmbpy) and cerium ammonium nitrate were obtained from Sigma-Aldrich Co., and used as received. The organic solvents for the synthesis were degassed and made anhydrous according to the standard procedures [31,32]. The synthesis of the $[\text{RuCl}_2(p\text{-cymene})]_2$ dimer and 4,4'-dinitro-2,2'-bipyridine (dnbpy) is described in the literature [33,34]. $^1\text{H-NMR}$ spectra were obtained with a Bruker WM-300 spectrometer. UV-vis spectra were recorded using Varian DMS 200 spectrophotometers, using Teflon-stoppered quartz cells with a path length of 1 cm.

Electrochemical investigations and cyclic voltammetry were performed with an Autolab PG-stat10 potentiostat controlled by GPES-4 software. A three electrode configuration pyrex glass cell was employed for electrochemical studies. The cell and glassware were decontaminated by boiling in a 1:2 mixture of concentrated nitric acid and sulfuric acid. The glass apparatus was then washed and boiled in ultra-pure water and dried in an oven. The cell was boiled 3 times in ultra-pure

water followed by thorough washing before each experiment. Solutions were prepared in ultra-pure water (Millipore MilliQ[®]) and electrochemical measurements were performed in deoxygenated aqueous solutions at room temperature.

The working electrode (WE) in the CV experiments was a freshly polished glassy carbon (GC) disk of 5.0 mm diameter, embedded in a PTFE shroud. A mirror finishing was achieved by polishing the GC disk mechanically with an aqueous slurry of 0.3, 0.1 and 0.05 μm alumina (Buehler Limited) successively, on a microcloth polishing fabric. After polishing, the GC disk was ultrasonically cleaned in Milli-Q (Millipore) water for 15 minutes after each polishing step and rinsed thoroughly with pure water. Platinum wire (thickness $l=1$ mm), shaped into a spiral, was used as a counter electrode (CE). The spiral platinum counter electrode was flame annealed and washed with pure water before placing it into the cell.

A mercury–mercury sulfate electrode (MMSE: $\text{Hg}/\text{Hg}_2\text{SO}_4/\text{K}_2\text{SO}_4$) was used as a reference electrode (RE) for the measurements in aqueous solution ($\text{pH} \leq 6$) and a silver–silver chloride electrode (SSCE: $\text{Ag}/\text{AgCl}/\text{KCl}$) was applied for the investigations in the neutral and higher pH aqueous solutions. All potentials are referred to the normal hydrogen electrode (NHE). The catalytic oxygen evolution was measured *in situ* in an air tight pyrex glass cell using a calibrated oxygen electrode connected with a digital O_2 meter (YSI, Inc., Model 550A) [7].

Synthesis

3.4.1. Chloro Complex $[(\text{cy})\text{Ru}^{\text{II}}(\text{bpy})\text{Cl}]\text{Cl}$ (**Ru-bpy**)

2,2'-bipyridine (bpy: 0.156 g, 1.0 mmol) in MeOH (15 mL) was added to a stirred mixture of $[\text{RuCl}_2(p\text{-cymene})]_2$ dimer (0.362 g, 0.5 mmol) in ab. MeOH (20 mL). The mixture was further stirred for 1.5 hours at 40–45 $^\circ\text{C}$. The solution was filtered with a sintered funnel of fine porosity and the solvent was evaporated under vacuum. The solid orange-yellow complex $[(\text{cy})\text{Ru}^{\text{II}}(\text{bpy})\text{Cl}]\text{Cl}$ thus obtained was

re-precipitated from acetone or MeOH by addition of ether/hexane. Yield 0.33 g, 71 %. ^1H NMR (CD_3OD , 295 K, δ ppm, J Hz): 9.49 (d, 2H, $\text{H}^{6,6'}$ _{bpy}, J 5.47); 8.51 (d, 2H, $\text{H}^{3,3'}$ _{bpy}, J 7.97); 8.23 (t, 2H, $\text{H}^{4,4'}$ _{bpy}, J 7.86); 7.76 (t, 2H, $\text{H}^{5,5'}$ _{bpy}, J 6.65); 6.13 (d, 2H, $\text{Ar}_{p\text{-cy}}$, J 6.33); 5.87 (d, 2H, $\text{Ar}_{p\text{-cy}}$, J 6.33); 2.63 (sep, 1H, $-\text{CH}(\text{CH}_3)_2_{p\text{-cy}}$); 2.27 (s, 3H, $\text{CH}_3_{p\text{-cy}}$); 1.17 (d, 6H, $-\text{CH}(\text{CH}_3)_2_{p\text{-cy}}$, J 6.91), Analysis found: C, 49.17%; H, 5.30%; N, 5.60%. Calculated: C, 50.0%; H, 5.04%; N, 5.83% for $\text{C}_{20}\text{H}_{22}\text{N}_2\text{Ru}_1\text{Cl}_2\cdot\text{H}_2\text{O}$ complex.

3.4.2. Chloro Complex $[(\text{cy})\text{Ru}^{\text{II}}(\text{dmbpy})\text{Cl}]\text{Cl}$ (**Ru-dmbpy**)

The orange-yellow chloro complex $[(\text{cy})\text{Ru}^{\text{II}}(\text{dmbpy})\text{Cl}]\text{Cl}$ was prepared in a similar manner as described above (section 3.4.1) using 4,4'-dimethyl-2,2'-bipyridine (dmbpy: 0.184 g, 1.0 mmol) instead of 2,2'-bipyridine. Yield 0.37 g, 76 %. ^1H NMR (CD_3OD , 295 K, δ ppm, J Hz): 9.26 (d, 2H, $\text{H}^{6,6'}$ _{dMebpy}, J 5.85); 8.37 (s, 2H, $\text{H}^{3,3'}$ _{dMebpy}); 7.58 (d, 2H, $\text{H}^{5,5'}$ _{dMebpy}, J 5.85); 2.62 (s, 6H, $4,4'-(\text{CH}_3)_2_{\text{dMebpy}}$); 6.06 (d, 2H, $\text{Ar}_{p\text{-cy}}$, J 6.33); 5.80 (d, 2H, $\text{Ar}_{p\text{-cy}}$, J 6.33); 2.60 (sep, 1H, $-\text{CH}(\text{CH}_3)_2_{p\text{-cy}}$); 2.26 (s, 3H, $\text{CH}_3_{p\text{-cy}}$); 1.03 (d, 6H, $-\text{CH}(\text{CH}_3)_2_{p\text{-cy}}$, J 6.91), Analysis found: C, 51.20%; H, 5.96%; N, 5.53%. Calculated: C, 51.97%; H, 5.55%; N, 5.51% for $\text{C}_{22}\text{H}_{26}\text{N}_2\text{Ru}_1\text{Cl}_2\cdot\text{H}_2\text{O}$ complex.

3.4.3. Chloro Complex $[(\text{cy})\text{Ru}^{\text{II}}(\text{dnbpy})\text{Cl}]\text{Cl}$ (**Ru-dnbpy**)

The orange-red chloro complex $[(\text{cy})\text{Ru}^{\text{II}}(\text{dnbpy})\text{Cl}]\text{Cl}$ was prepared in a similar manner as described above (section 3.4.1) using 4,4'-dinitro-2,2'-bipyridine (dnbpy: 0.246 g, 1.0 mmol) instead of 2,2'-bipyridine. Yield 0.43 g, 78 %. ^1H NMR (CD_3OD , 295 K, δ ppm, J Hz): 9.88 (d, 2H, $\text{H}^{6,6'}$ _{dnbpy}, J 6.81); 9.51 (s, 2H, $\text{H}^{3,3'}$ _{dnbpy}); 8.53 (dd, 2H, $\text{H}^{5,5'}$ _{dnbpy}, J 2.28, J 6.25); 6.28 (d, 2H, $\text{Ar}_{p\text{-cy}}$, J 6.37); 6.05 (d, 2H, $\text{Ar}_{p\text{-cy}}$, J 6.37); 2.75 (sep, 1H, $-\text{CH}(\text{CH}_3)_2_{p\text{-cy}}$); 2.28 (s, 3H, $\text{CH}_3_{p\text{-cy}}$); 1.11 (d, 6H, $-\text{CH}(\text{CH}_3)_2_{p\text{-cy}}$, J 6.91), Analysis found: C, 41.43%; H, 4.13%; N, 9.50%. Calculated: C, 42.11%; H, 3.89%; N, 9.82% for $\text{C}_{20}\text{H}_{20}\text{N}_4\text{O}_4\text{Ru}_1\text{Cl}_2\cdot\text{H}_2\text{O}$ complex.

3.4.4. Chloro Complex [(cy)Ru^{II}(phen)Cl]Cl (**Ru-phen**)

The orange-yellow chloro complex [(cy)Ru^{II}(phen)Cl]Cl was prepared in a similar manner as described above (section 3.4.1) using 1,10-phenanthroline (phen: 0.18 g, 1.0 mmol) instead of 2,2'-bipyridine. Yield 0.34 g, 70 %. ¹H NMR (CD₃OD, 295 K, δ ppm, J Hz): 9.84 (dd, 2H, H^{2,9}_{phen}, J 1.14, J 5.27); 8.83 (dd, 2H, H^{4,7}_{phen}, J 1.14, J 8.25); 8.2 (s, 2H, H^{5,6}_{phen}); 8.11 (dd, 2H, H^{3,8}_{phen}, J 5.31, J 8.38); 6.24 (d, 2H, Ar_{p-cy}, J 6.35); 6.0 (d, 2H, Ar_{p-cy}, J 6.35); 2.66 (sep, 1H, -CH(CH₃)_{2 p-cy}); 2.26 (s, 3H, CH_{3 p-cy}); 0.98 (d, 6H, -CH(CH₃)_{2 p-cy}, J 6.91), Analysis found: C, 50.32%; H, 5.21%; N, 5.31%. Calculated: C, 50.58%; H, 5.02%; N, 5.36% for C₂₂H₂₂N₂RuCl₂·2H₂O complex.

3.4.5. Chloro Complex [(cy)Ru^{II}(bpm)Cl]Cl (**Ru-bpm**)

The orange-brown chloro complex [(cy)Ru^{II}(bpm)Cl]Cl was prepared in a similar manner as described above (section 3.4.1) using 2,2'-bipyrimidine (bpm: 0.158 g, 1.0 mmol) instead of 2,2'-bipyridine. Yield 0.31 g, 67 %. ¹H NMR (CD₃OD, 295 K, δ ppm, J Hz): 9.8 (dd, 2H, H^{6,6'}_{bpm}, J 1.96, J 5.76); 9.28 (dd, 2H, H^{4,4'}_{bpm}, J 1.96, J 4.77); 7.96 (t, 2H, H^{5,5'}_{bpm}, J 5.26); 6.22 (d, 2H, Ar_{p-cy}, J 6.43); 6.01 (d, 2H, Ar_{p-cy}, J 6.43); 2.79 (sep, 1H, -CH(CH₃)_{2 p-cy}); 2.25 (s, 3H, CH_{3 p-cy}); 1.17 (d, 6H, -CH(CH₃)_{2 p-cy}, J 6.91), Analysis found: C, 43.61%; H, 4.89%; N, 11.40%. Calculated: C, 43.97%; H, 4.71%; N, 11.39% for C₁₈H₂₀N₄RuCl₂·1.5H₂O complex.

3.4.6. General Synthesis of the Aqua Complexes: [(cy)Ru^{II}(L)-OH₂]²⁺ (Cat.**Ru-L**)

The chloro complexes [(cy)Ru^{II}(L)Cl]⁺ (**Ru-L**) were converted into the aqua (OH₂) catalysts [(cy)Ru^{II}(L)-OH₂]²⁺ (Cat.**Ru-L**) by stirring with aqueous solution containing 2.1 eq. of AgNO₃ or silver hexafluorophosphate in methanol (1:1, H₂O/MeOH) for 30 minutes. The white precipitates were filtered off and the solvent mixture was evaporated under vacuum. The yellow solid aqua complexes

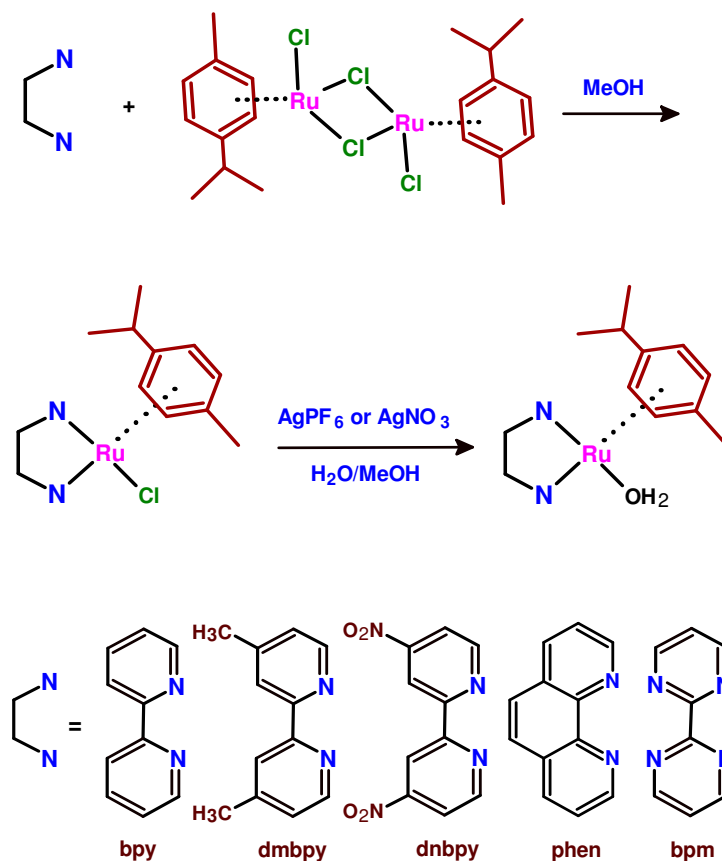
thus obtained were recrystallized from acetone or MeOH by addition of ether/hexane.

3.4.7. Direct Synthesis of the Aqua Complexes: $[(\text{cy})\text{Ru}^{\text{II}}(\text{L})\text{-OH}_2]^{2+}$
(Cat.**Ru**-L)

Dinitrogen ligands (L) (1.0 mmol) were dissolved in 15 mL MeOH/H₂O and added to aqueous tri-aqua $[(\text{Ru})(\text{cy})\text{-(OH}_2)_3]^{2+}$ (1.0 mmol). The mixture was stirred for 5 hours at 65 °C giving a yellow solution. The solvent was evaporated to yield a yellow solid $[(\text{cy})\text{Ru}^{\text{II}}(\text{L})\text{-OH}_2]^{2+}$ (Cat.**Ru**-L) that was further dried in vacuo. The solid pale yellow complex thus obtained was recrystallized from MeOH by addition of ether/hexane.

The rapid *in situ* aqua (OH₂) exchange in the complex $[(\text{cy})\text{Ru}^{\text{II}}(\text{L})\text{Cl}]^+$ also occurred when the complex is mixed with the 0.1 M aqueous acidic solution for a few minutes. The aqua exchange was monitored by following the colour change of the solution from orange to yellow visually or by UV-Vis spectral investigation (Fig. 3.2).

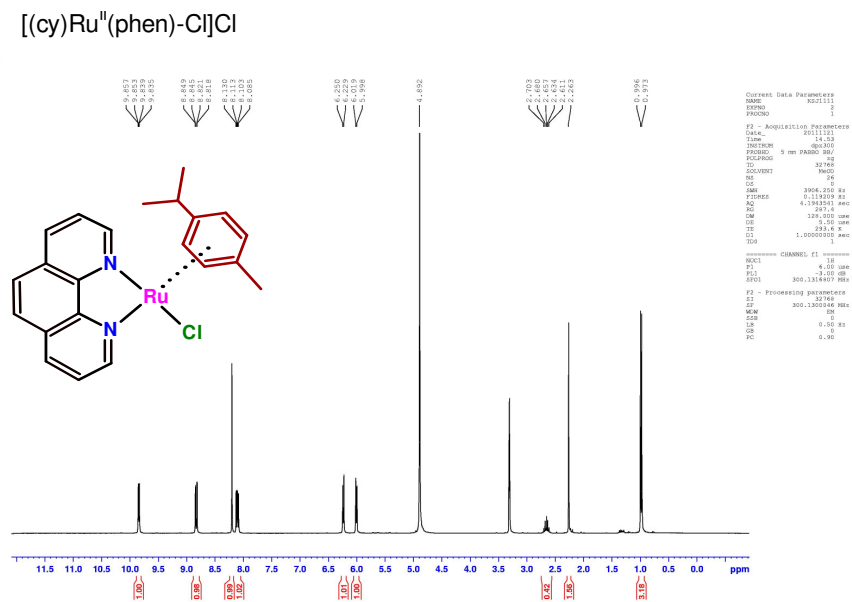
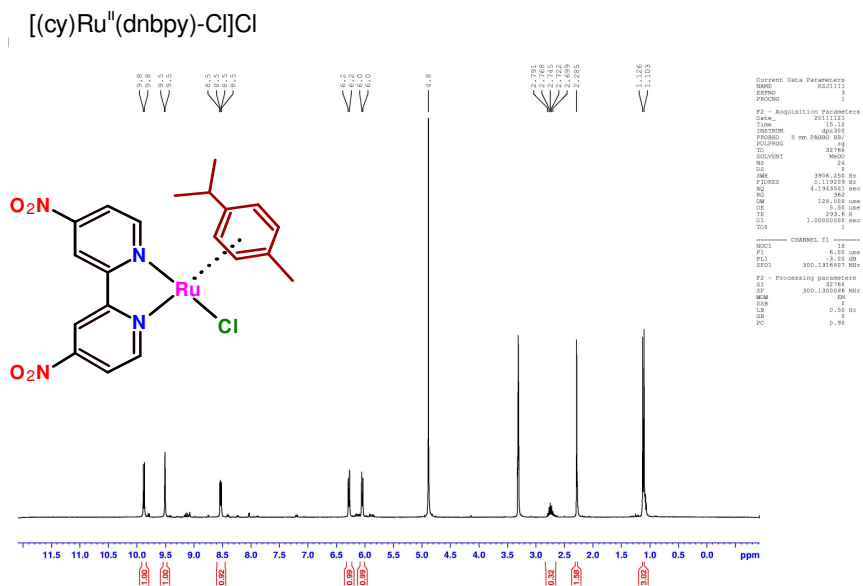
Scheme 3.2. Schematic representation of the synthesis route for the *p*-cymene ruthenium derived bipyridine, 4,4'-disubstituted-2,2'-bipyridine, phenanthroline and 2,2'-bipyrimidine mono metal complexes.



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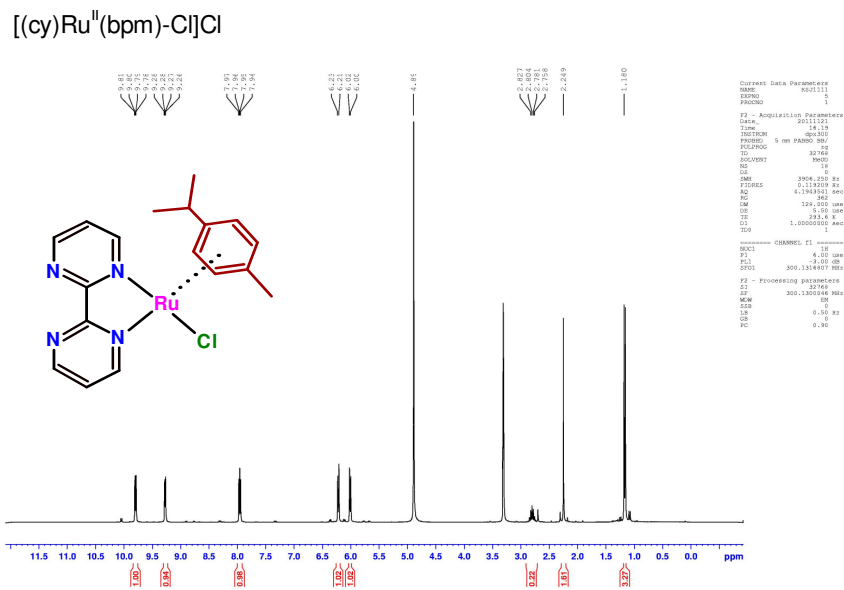


Figure A3.1. Proton NMR spectra of the complexes **Ru-bpy**, **Ru-bdmpy**, **Ru-dnbpy**, **Ru-phen** and **Ru-bpm**.

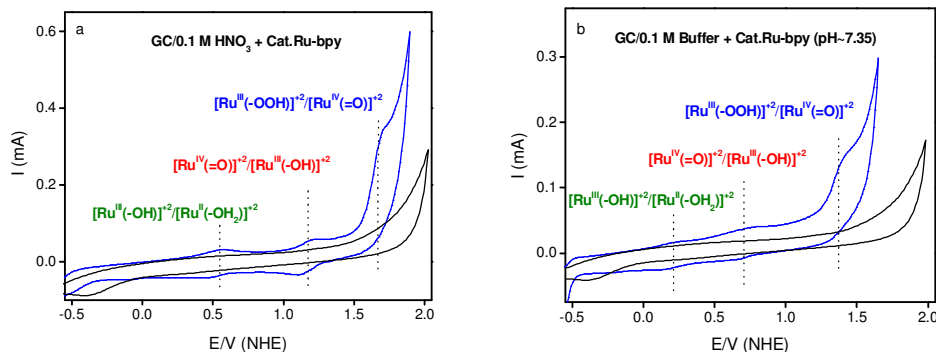


Figure A3.2. Cyclic voltammograms of Cat.**Ru**-bpy (2.5 mM) at glassy carbon disk working electrode in 0.1 M (a) HNO_3 and (b) buffer (pH~7.35) solutions showing $[\text{Ru}^{\text{III}}(-\text{OH})]^{2+}/[\text{Ru}^{\text{II}}(-\text{OH}_2)]^{2+}$ and $[\text{Ru}^{\text{IV}}(=\text{O})]^{2+}/[\text{Ru}^{\text{III}}(-\text{OH})]^{2+}$ reversible couples. (Scan rate was 100 mV/sec; glassy carbon disk diameter $d=5$ mm).

Figure A3.3.

Spectral investigation ascribed to the consecutive oxidation of $[(\text{cy})\text{Ru}(\text{bpm})-(\text{OH}_2)]^{2+}$ catalyst (green line) into $[\text{Ru}^{\text{III}}-(\text{OH})]^{2+}$, (red line) $[\text{Ru}^{\text{IV}}(=\text{O})]^{2+}$, (blue line) $[\text{Ru}^{\text{III}}-(\text{OOH})]^{2+}$ and (purple line) $[\text{Ru}^{\text{IV}}-(\text{OO})]^{2+}$ in 0.1 M aqueous HNO_3 using quantitative $\text{Ce}(\text{IV})$ solution.

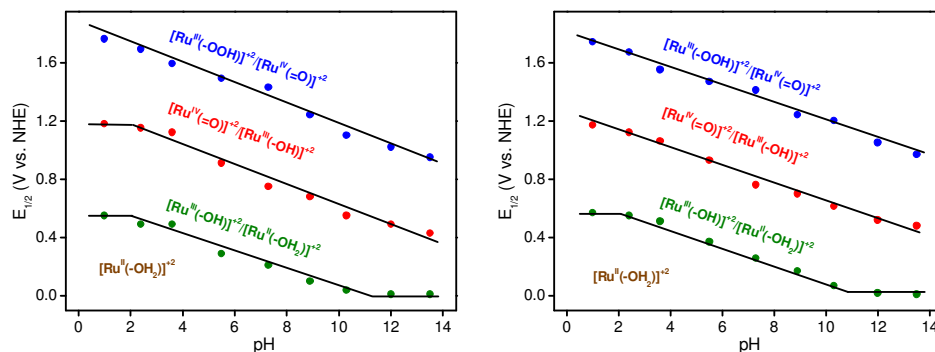
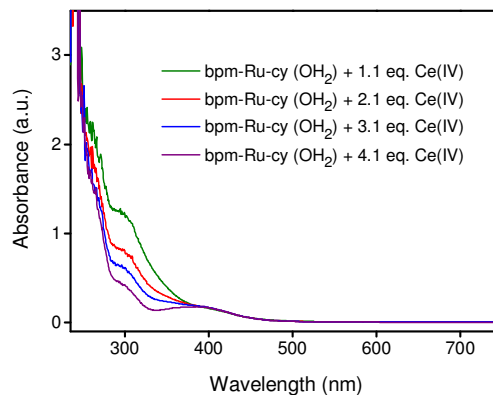


Figure A3.4. (Left) Potential vs pH plot (Pourbaix diagram) for $[(\text{phen})\text{Ru}^{\text{II}}(\text{cy})\text{OH}_2]^{2+}$ and (right) $[(\text{bpm})\text{Ru}^{\text{II}}(\text{cy})\text{OH}_2]^{2+}$ showing $[\text{Ru}^{\text{III}}(\text{OH})]^{2+}/[\text{Ru}^{\text{II}}(\text{OH}_2)]^{2+}$, $[\text{Ru}^{\text{IV}}(=\text{O})]^{2+}/[\text{Ru}^{\text{III}}(\text{OH})]^{2+}$ and $[\text{Ru}^{\text{III}}(\text{OOH})]^{2+}/[\text{Ru}^{\text{IV}}(=\text{O})]^{2+}$ transitions generated at glassy carbon disk (diameter $d=5\text{mm}$) working electrode in 0.1 M aqueous solutions.

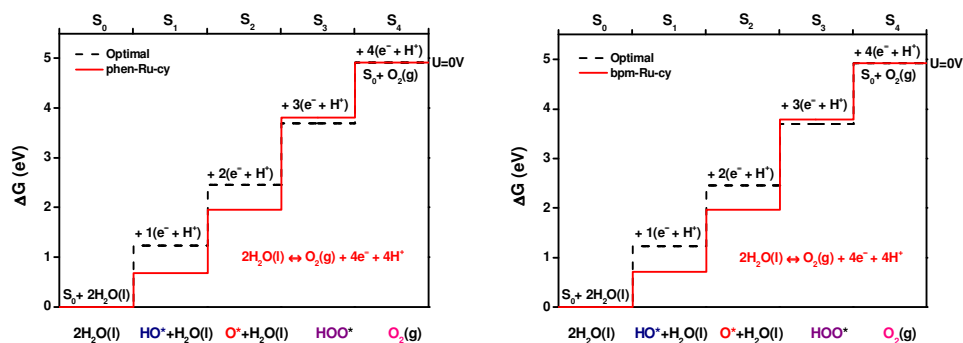


Figure A3.5. Relative Gibbs free energies (ΔG) of reactive species and intermediates (horizontal lines) during water splitting and oxygen generation for (Left) $[(\text{phen})\text{Ru}^{\text{II}}(\text{cy})\text{OH}_2]^{2+}$ ($\Delta G = 0.68, 1.28, 1.85 \text{ eV}$) and (right) $[(\text{bpm})\text{Ru}^{\text{II}}(\text{cy})\text{OH}_2]^{2+}$ ($\Delta G = 0.71, 1.26, 1.82 \text{ eV}$), compared with the free energy profiles for the reaction coordinate of an optimal catalyst with four steps each of 1.23 eV [13,16].

Table A3.1. Initial rates for oxygen generation catalyzed by [(cy)Ru^{II}(N-N)-OH₂]²⁺ complexes in argon-purged 0.1 M HNO₃ aqueous solutions using 350 eq. of Ce(IV).

Catalyst	Formula	Initial rate (t.o.hour ⁻¹) ^a	TON ^b
Cat. Ru -bpy	(bpy)Ru ^{II} (cy)-OH ₂	29.3	46.2
Cat. Ru -dmbpy	(dmbpy)Ru ^{II} (cy)-OH ₂	15	39.4
Cat. Ru -dnbpy	(dnbpy)Ru ^{II} (cy)-OH ₂	31.7	42.9
Cat. Ru -phen	(phen)Ru ^{II} (cy)-OH ₂	12	30.1
Cat. Ru -bpm	(bpm)Ru ^{II} (cy)-OH ₂	42	53

^a Turnovers (t.o.) obtained in first hour of catalysis and ^b total turnover number obtained during 5 hours of catalysis operation.

